Tasks 6.1 and 6.2: Phase Distributions and Secondary Formation During Winter in the San Joaquin Valley

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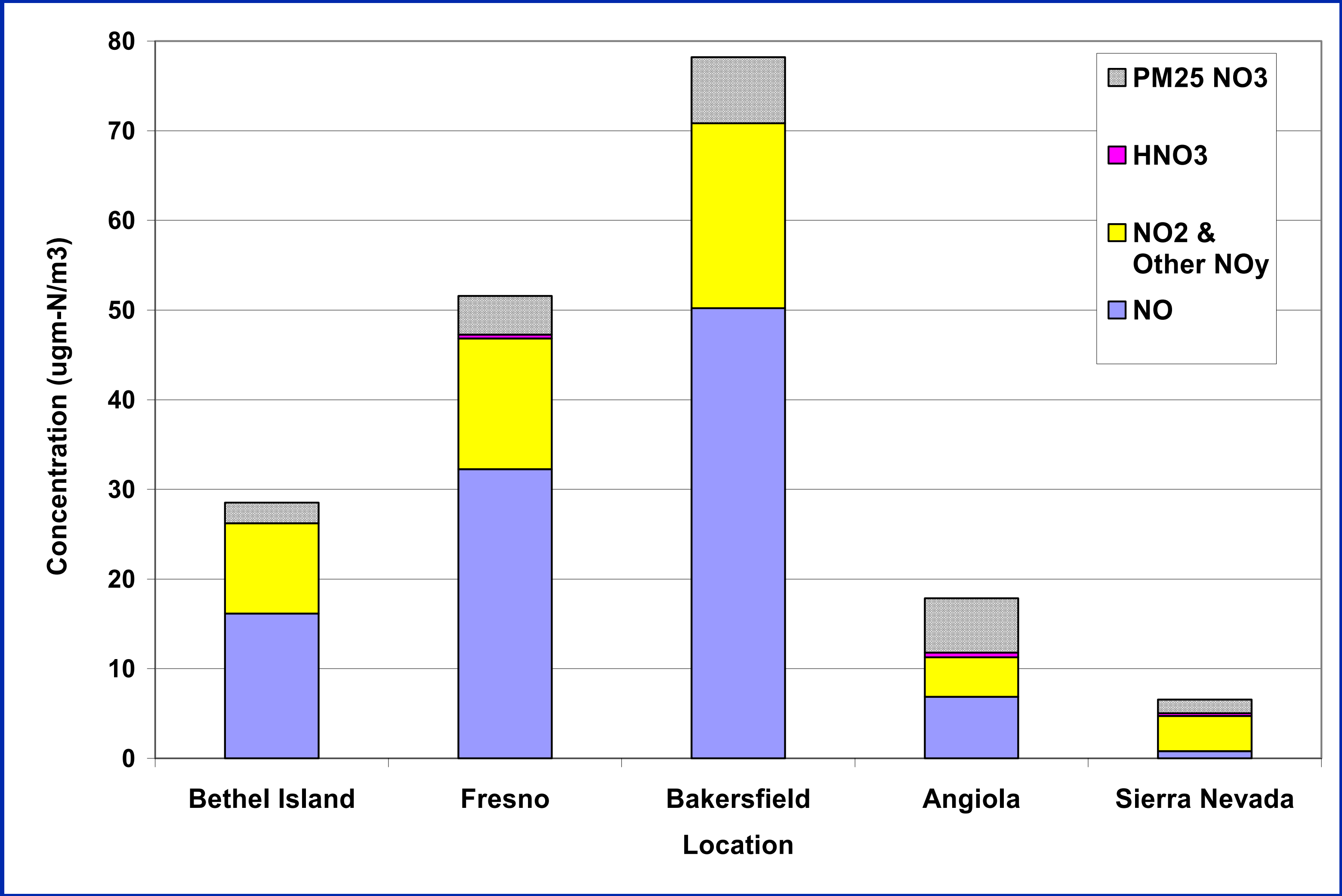
Phase Partitioning-Related Questions

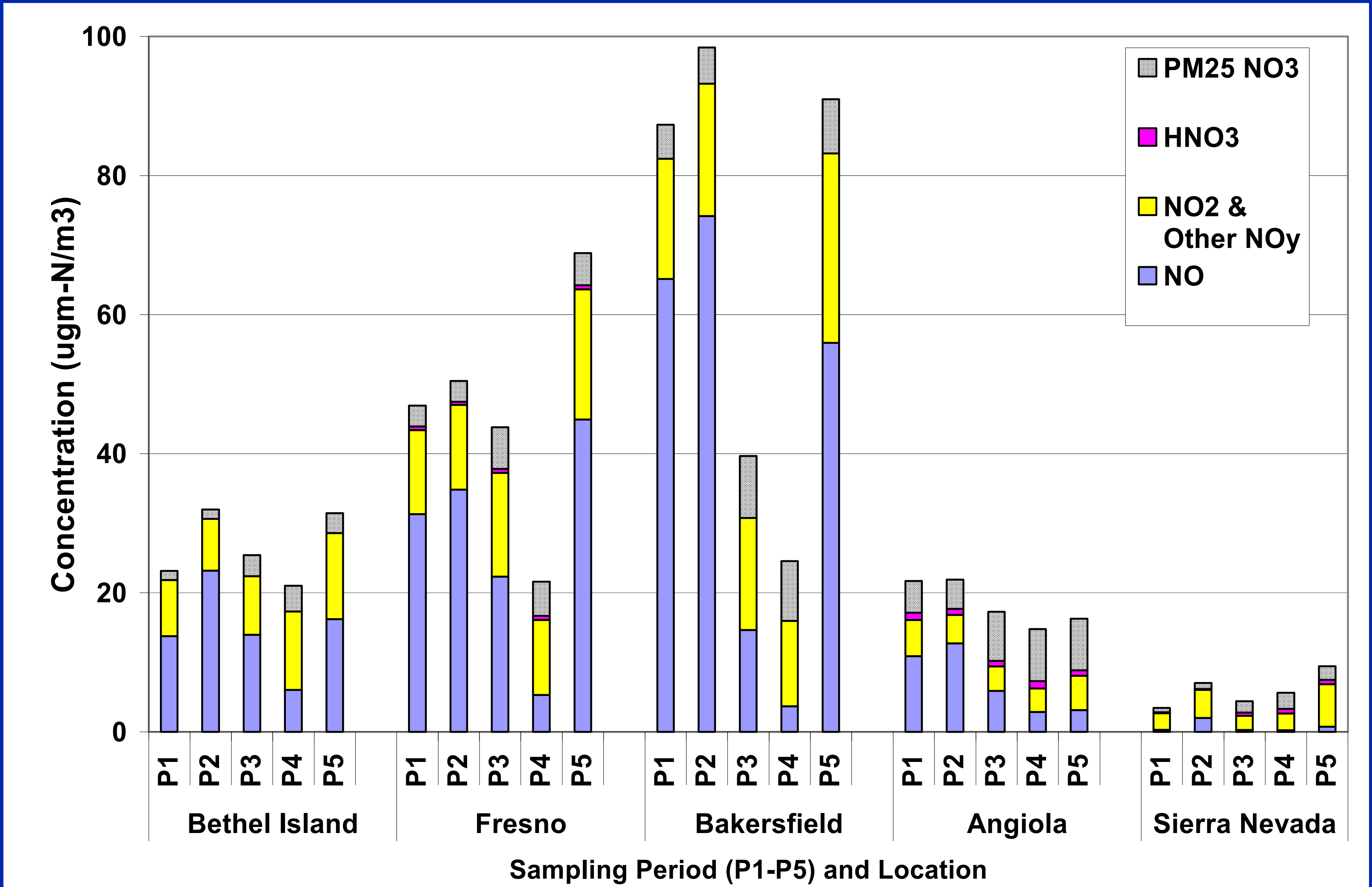
- What is the distribution of PM and precursor species among the gas, liquid, and aerosol phases?
- How do the phase distributions and chemical and physical mechanisms vary in space and time?
- What chemical and physical mechanisms contribute to the observed phase distributions?

Average Phase Distribution of NO_x-Related Species CRPAQS Winter 2000/2001 IOP Days



HNO_3 data were not available at Bethel Island and Bakersfield

Average Phase Distribution of NO_x-Related Species by Period
CRPAQS Winter 2000/2001 IOP Days



Periods: P1 = 0-5, P2 = 5-10, P3 = 10-13, P4 = 13-16, P5 = 16-24

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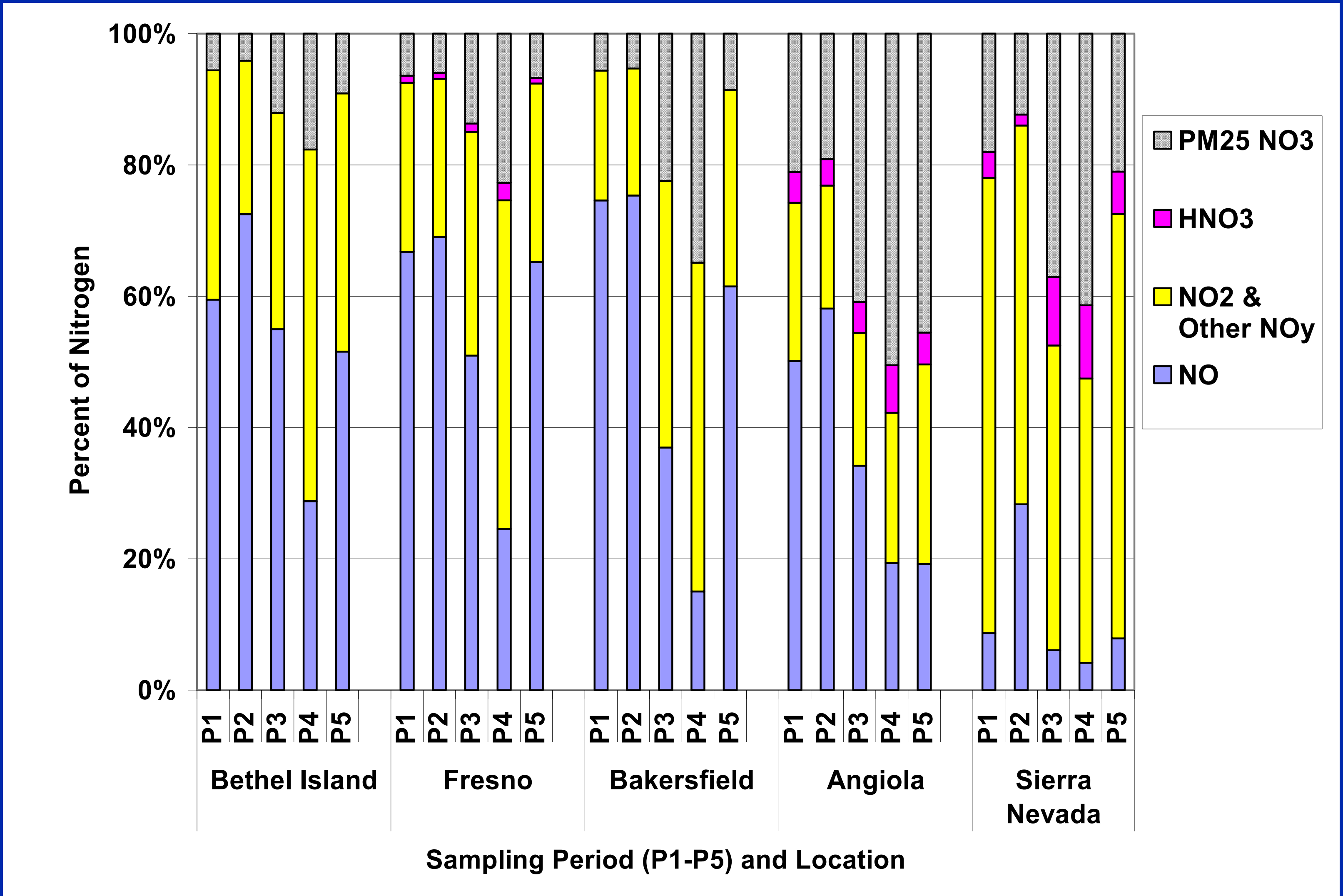
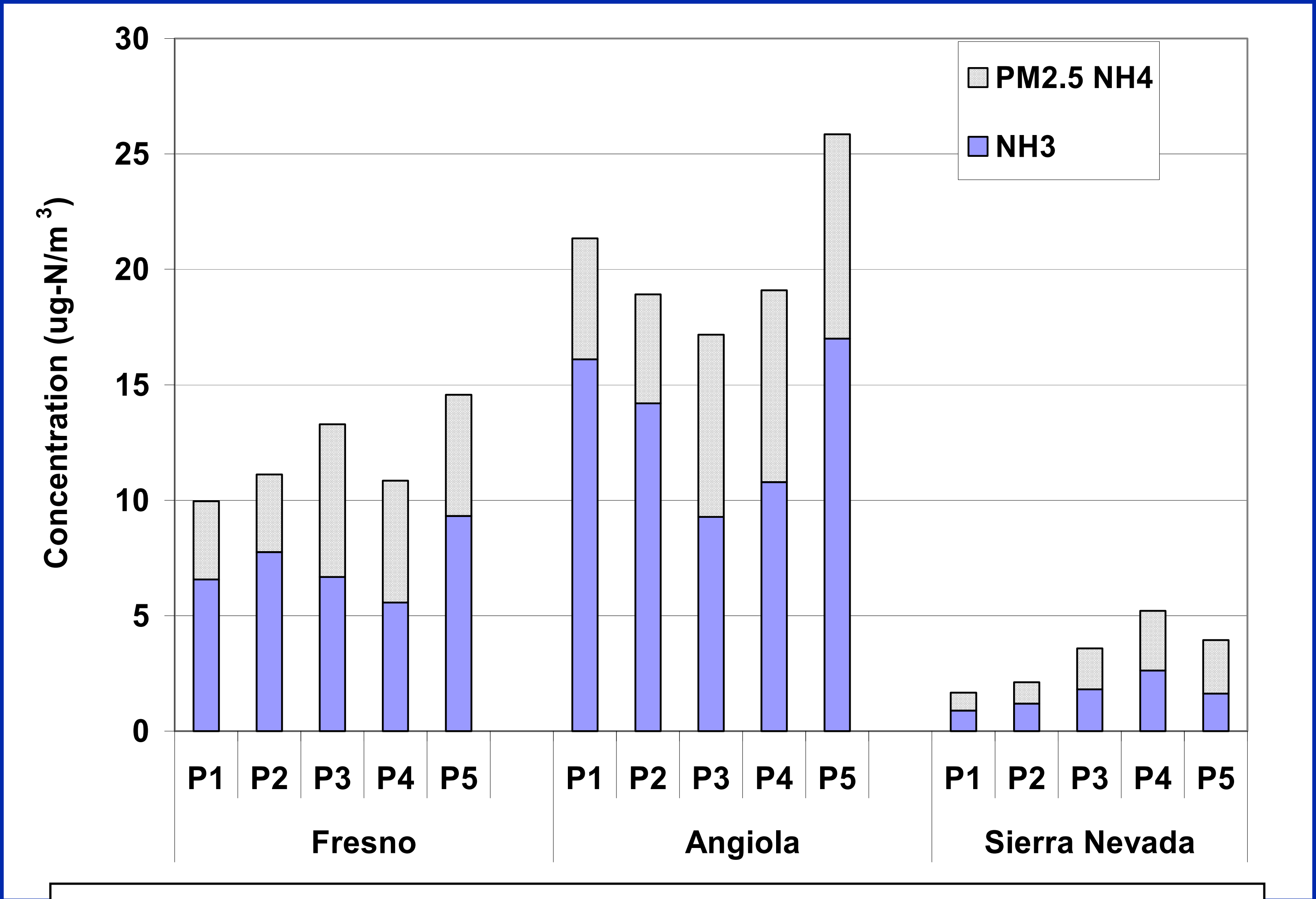
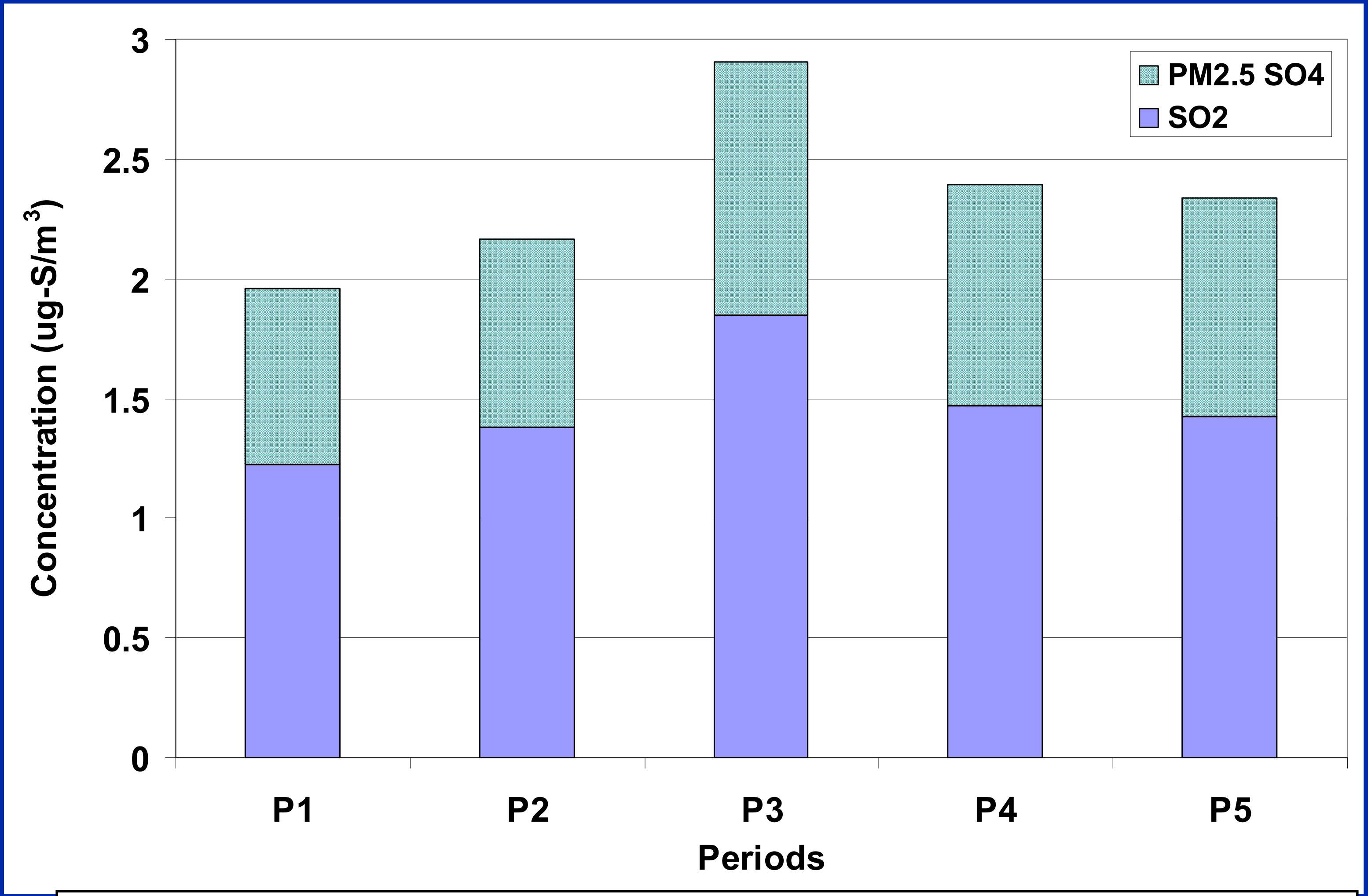


Average Phase Distribution of NH_3-Related Species by Period
CRPAQS Winter 2000/2001 IOP Days



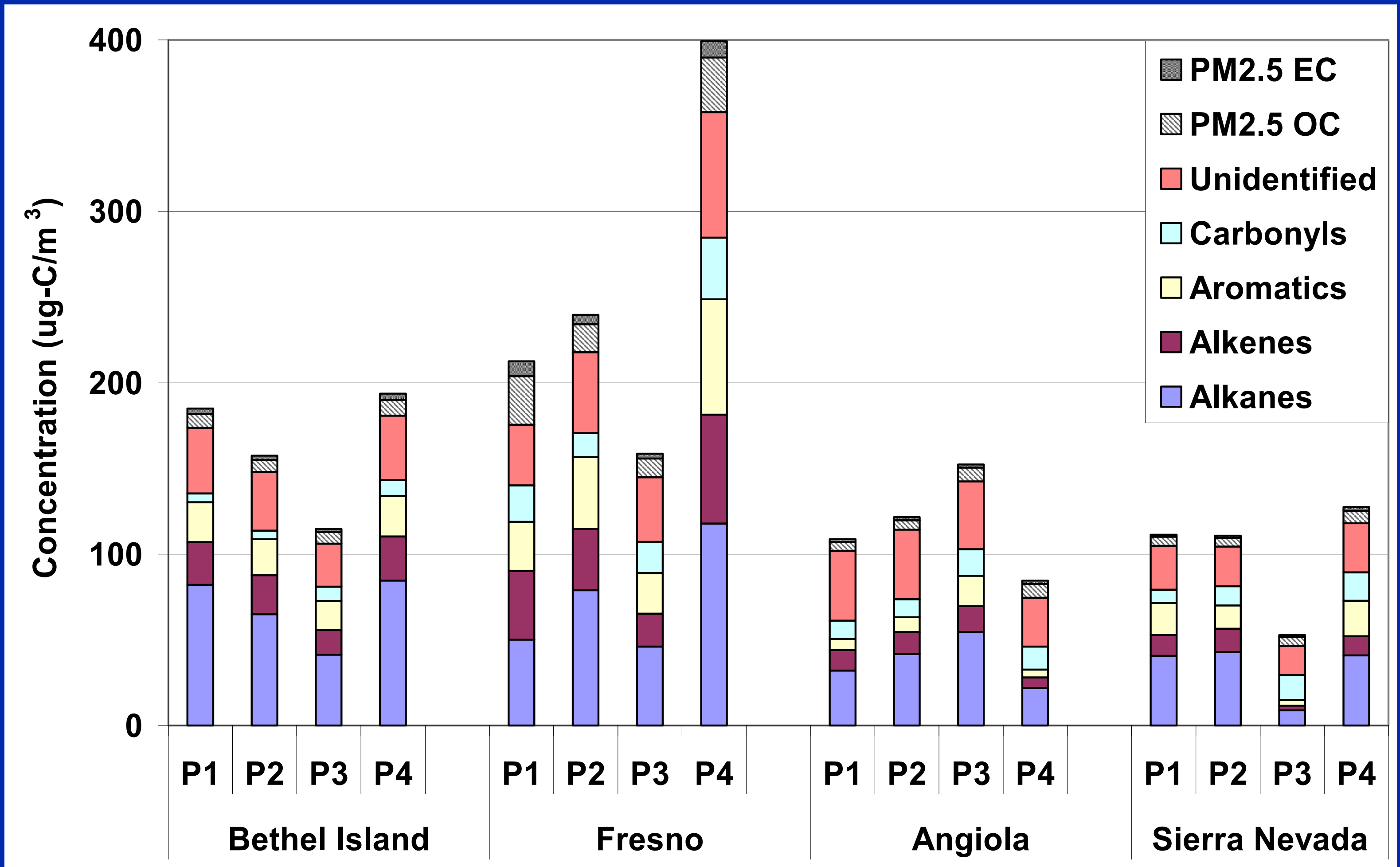
Periods: P1 = 0-5, P2 = 5-10, P3 = 10-13, P4 = 13-16, P5 = 16-24

Average Phase Distribution of SO_2-Related Species by Period In Bakersfield - Winter 2000/2001 IOP Days



Periods: P1 = 0-5, P2 = 5-10, P3 = 10-13, P4 = 13-16, P5 = 16-24

Average Phase Distribution of Organics by Period CRPAQS Winter 2000/2001 IOP Days



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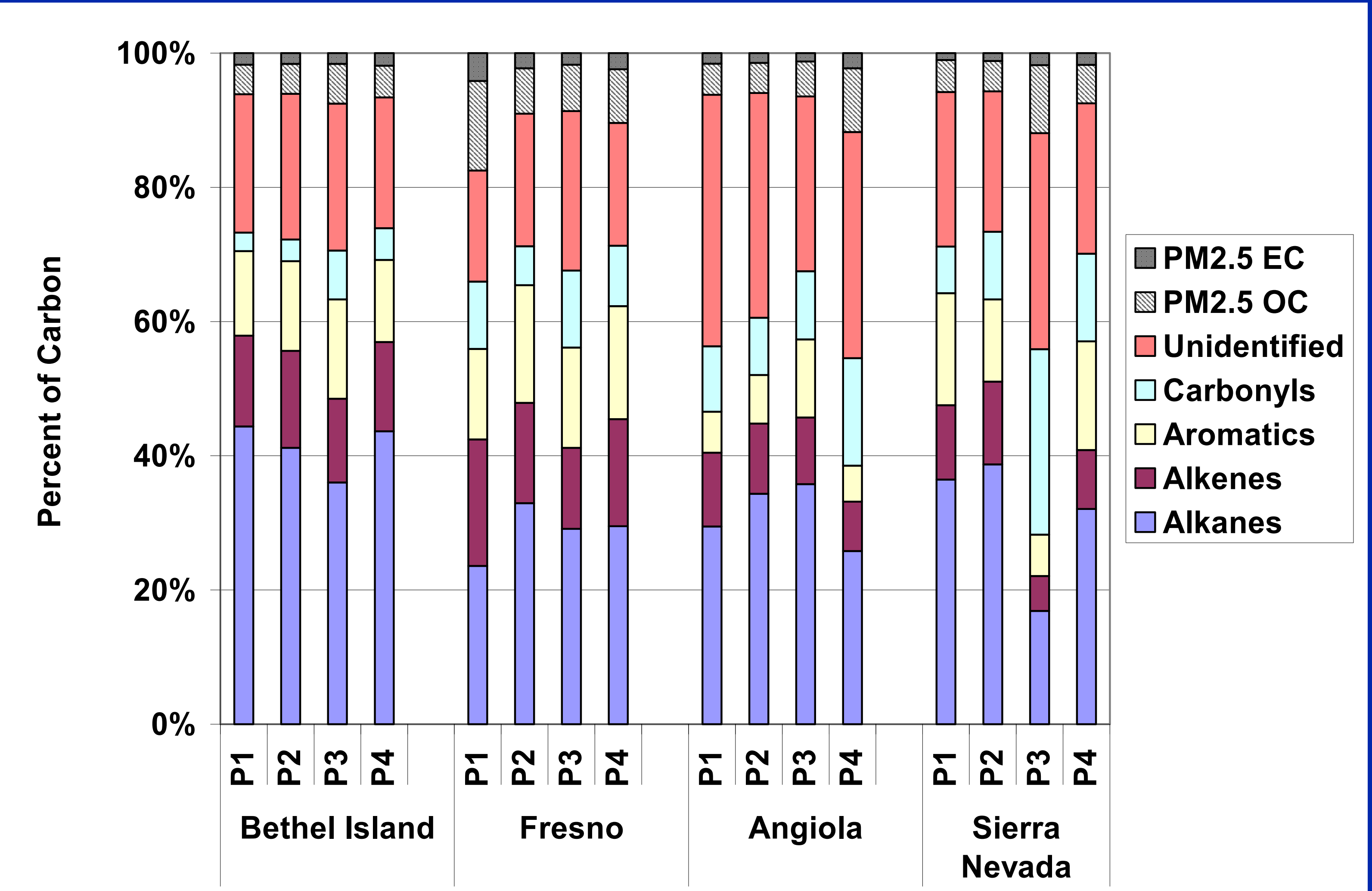

Periods: P1 = 0-5, P2 = 5-10, P3 = 10-16, P4 = 16 -24

Secondary Formation Questions

- Where and when do precursors (VOC, NO_x, NH_3, HNO_3, and SO_2) limit the formation of secondary sulfates and nitrates?
- How is NO_x oxidized to nitric acid?
- How much ozone and precursor species are above the valleywide layer and how much gets into the mixed layer?

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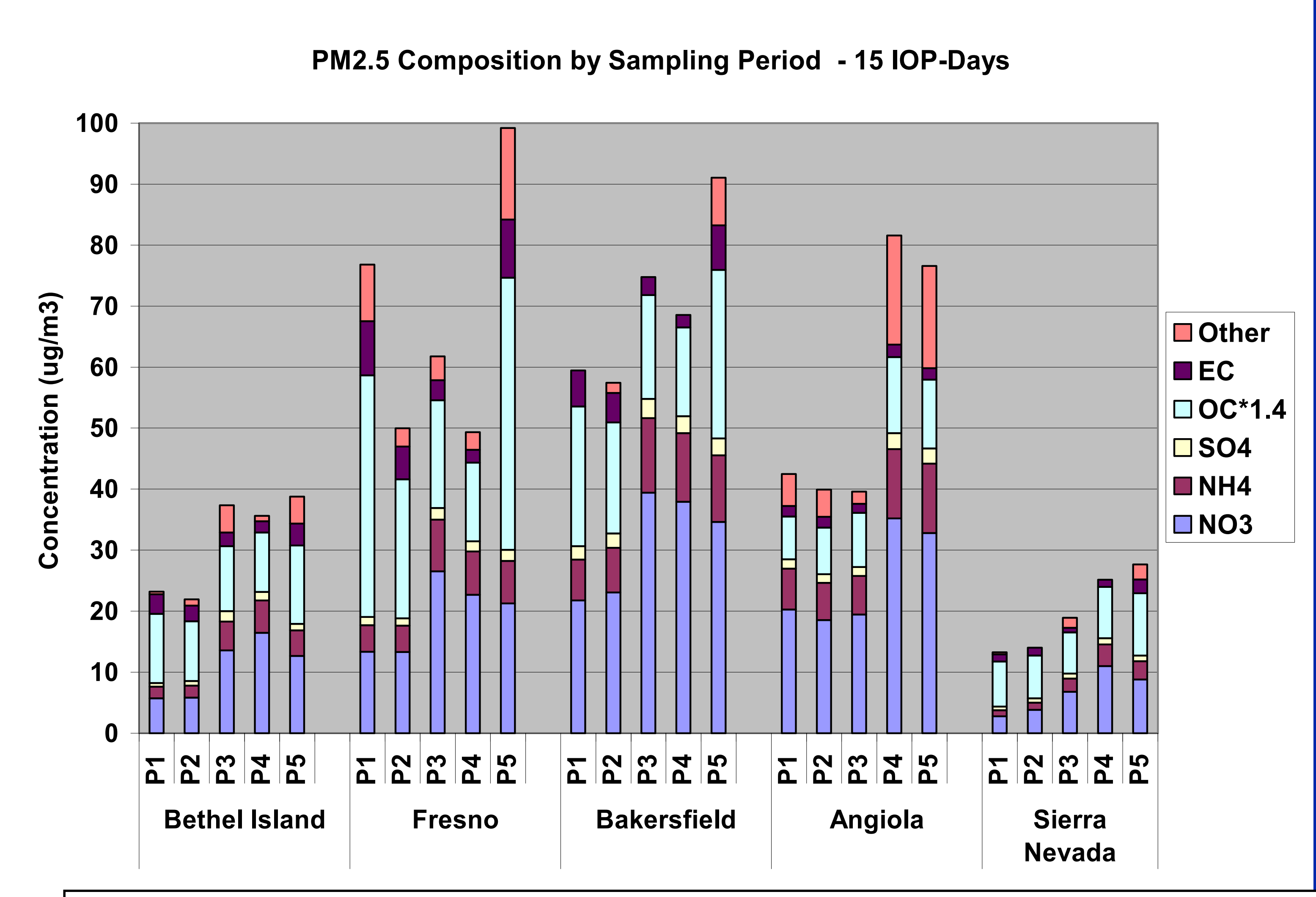
Important Observations for Winter $PM_{2.5}$ in SJV

- NH_4NO_3 is generally the most abundant chemical component in $PM_{2.5}$ followed by carbonaceous material (OC+EC)
- NH_4NO_3 concentrations are limited by the rate of HNO_3 formation, rather than by the availability of NH_3
- HNO_3 is formed via daytime photochemistry and a nighttime chemistry aloft

Important Observations for Winter $PM_{2.5}$ in SJV

- Primary NO_x and OC+EC emissions are important contributors
- Secondary Organic Aerosol (SOA) formation from VOC emissions is important in winter, but not as important as primary OC+EC emissions
- Daytime photochemistry is VOC-, sunlight-, and background-ozone-limited in winter. This is a nonlinear regime for the gas-phase chemistry

Diurnal Patterns of $PM_{2.5}$ Components in Winter



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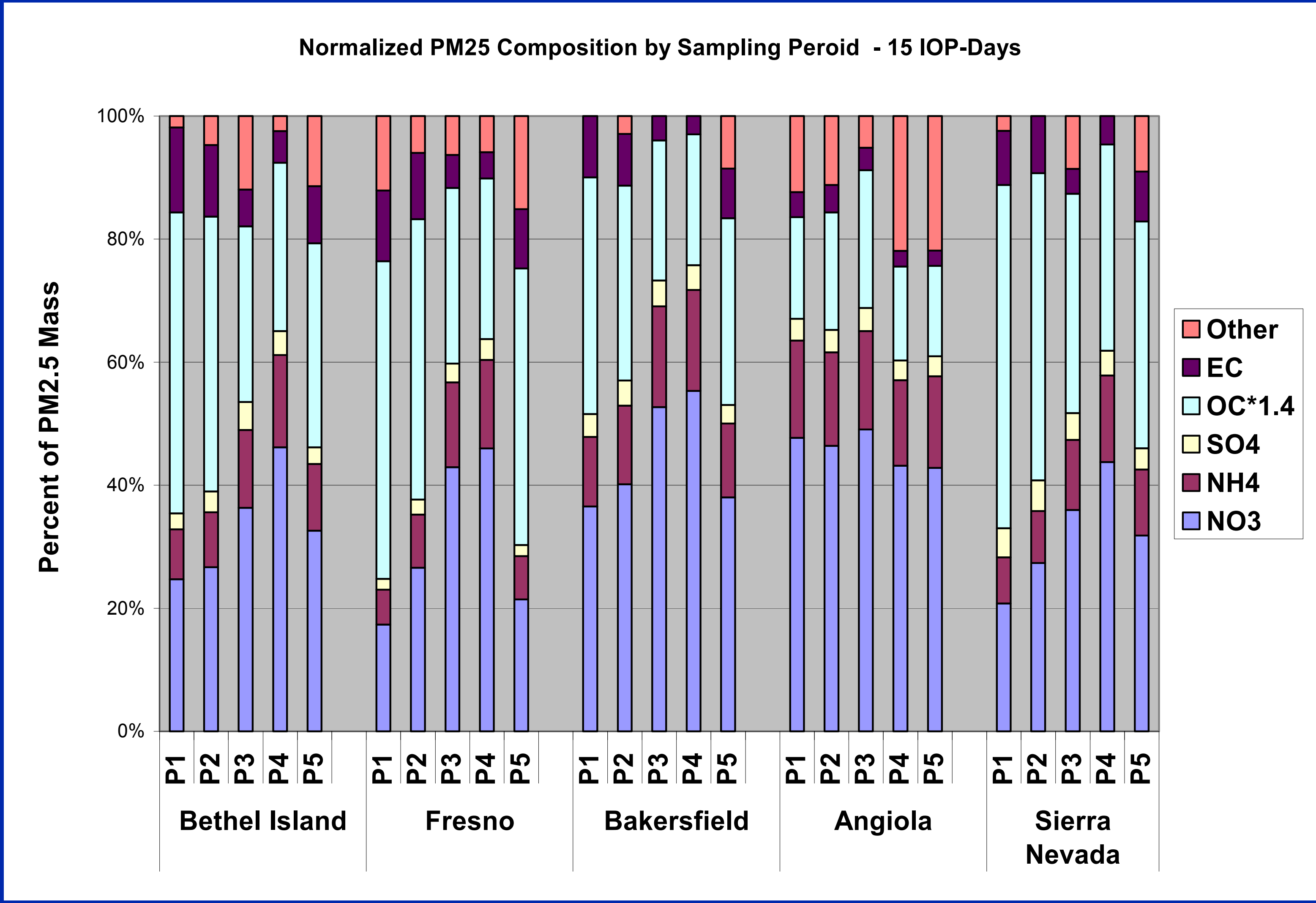
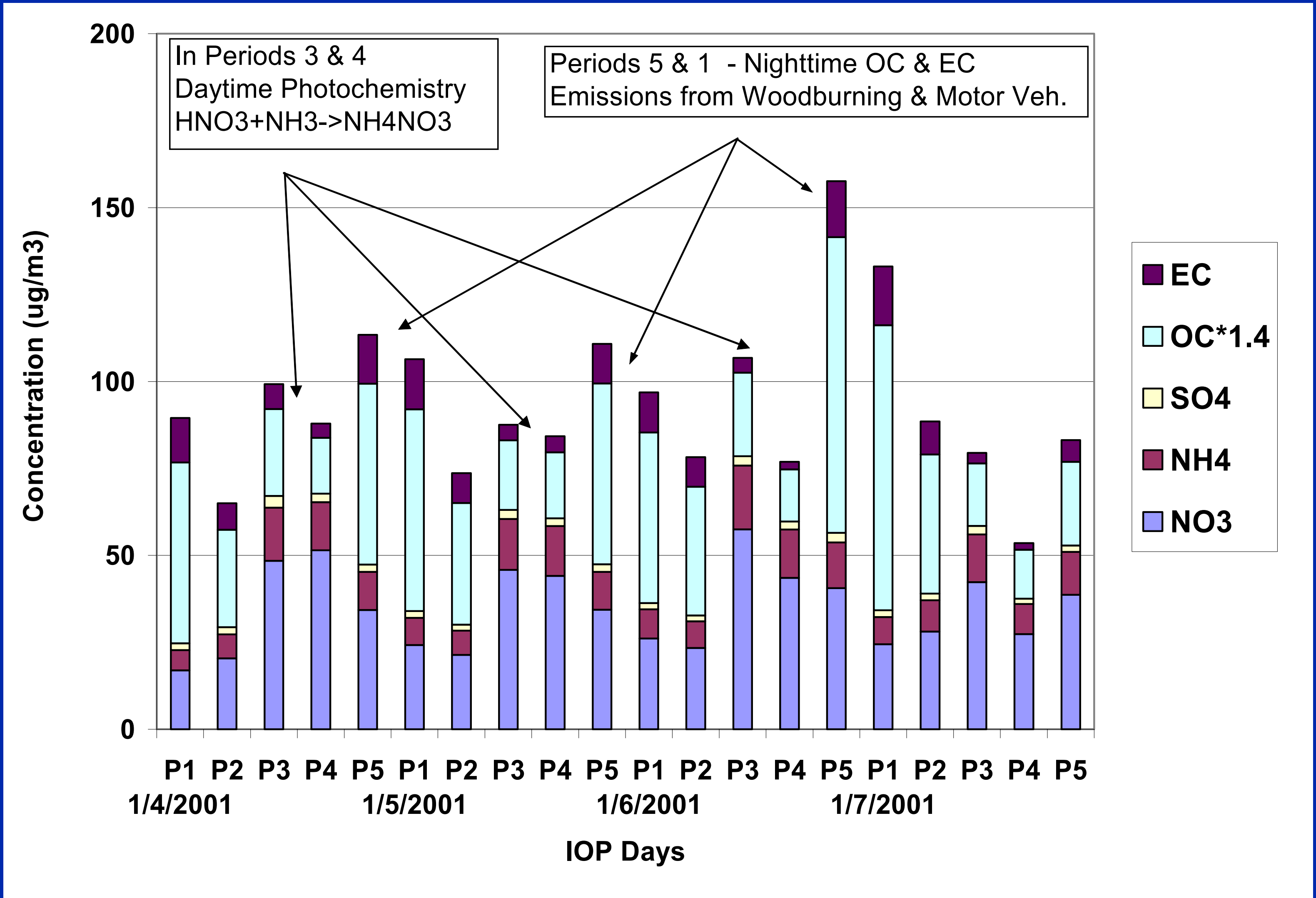
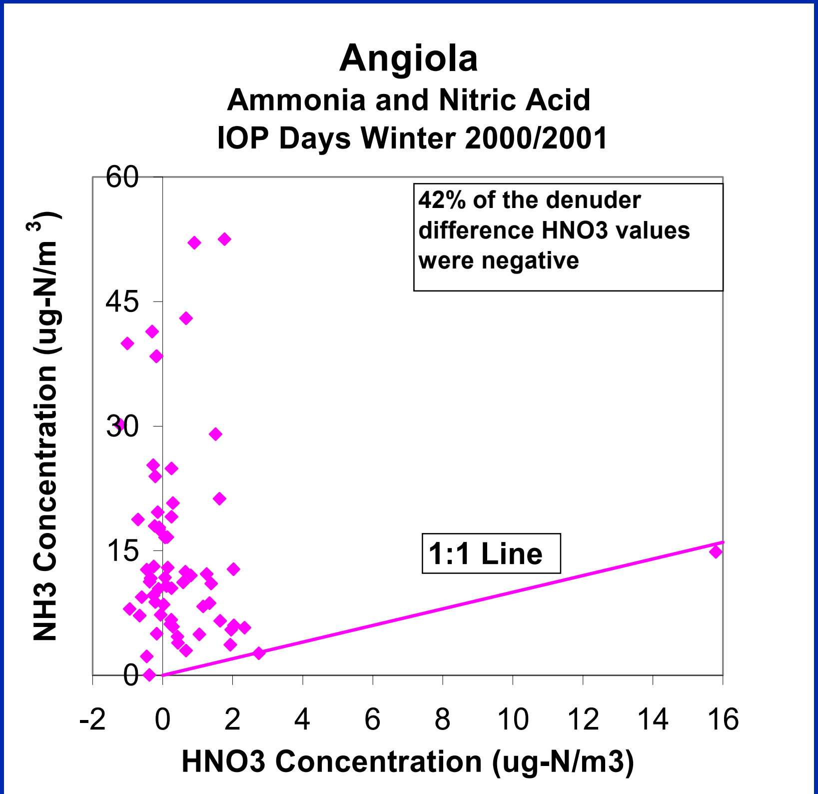
Diurnal Patterns of $PM_{2.5}$ Components in Winter

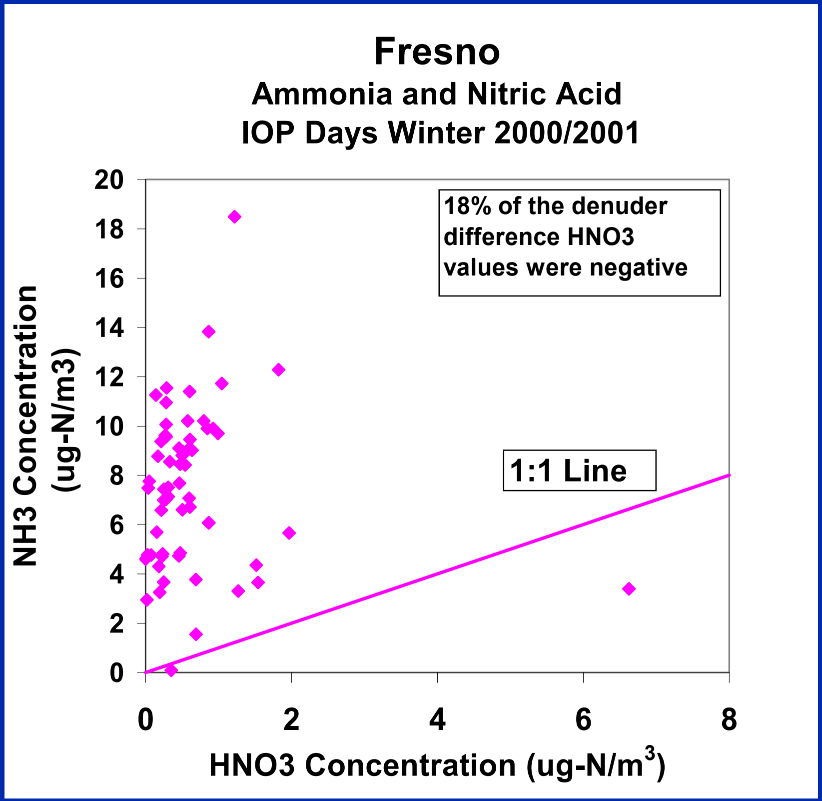


Fresno $PM_{2.5}$ 1/4/01 – 1/7/01



Nitrate Formation Is Not Likely to be Limited by Ammonia Availability





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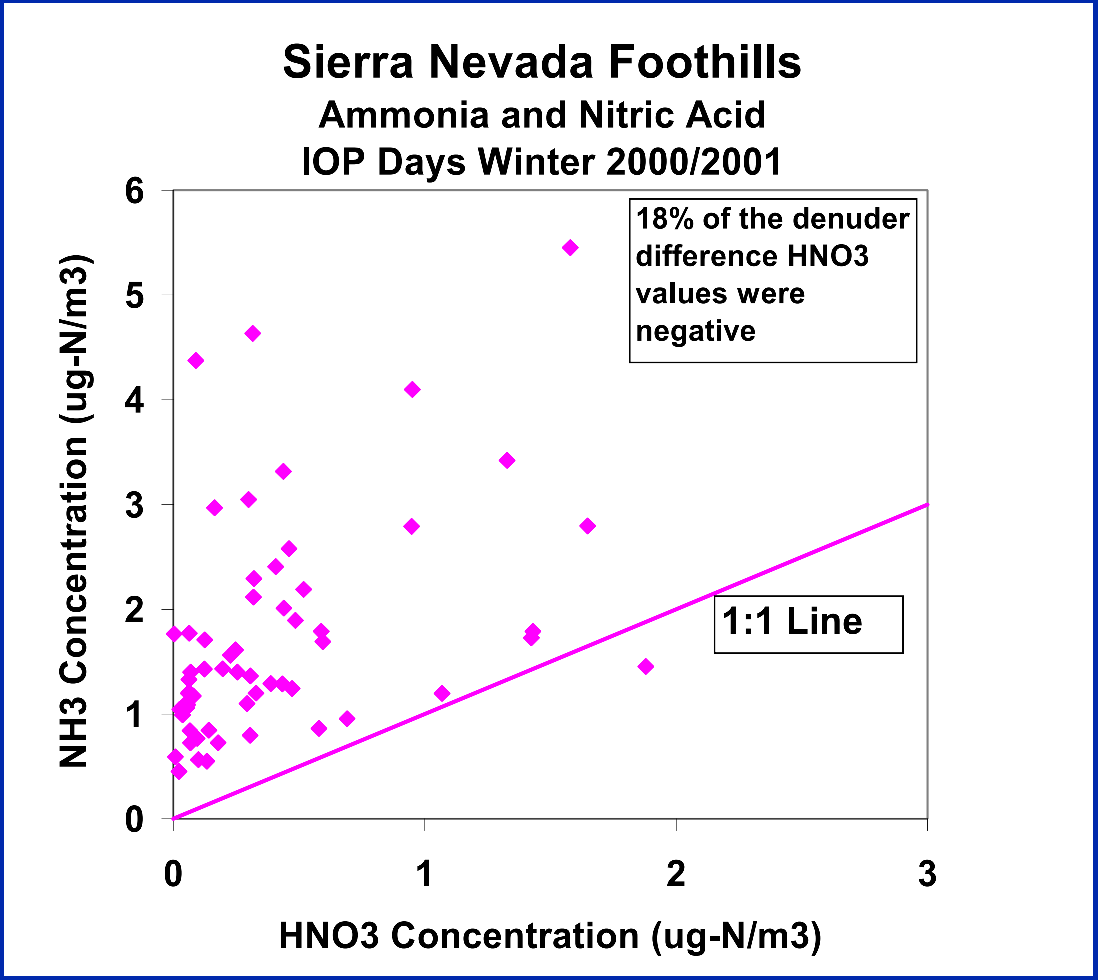
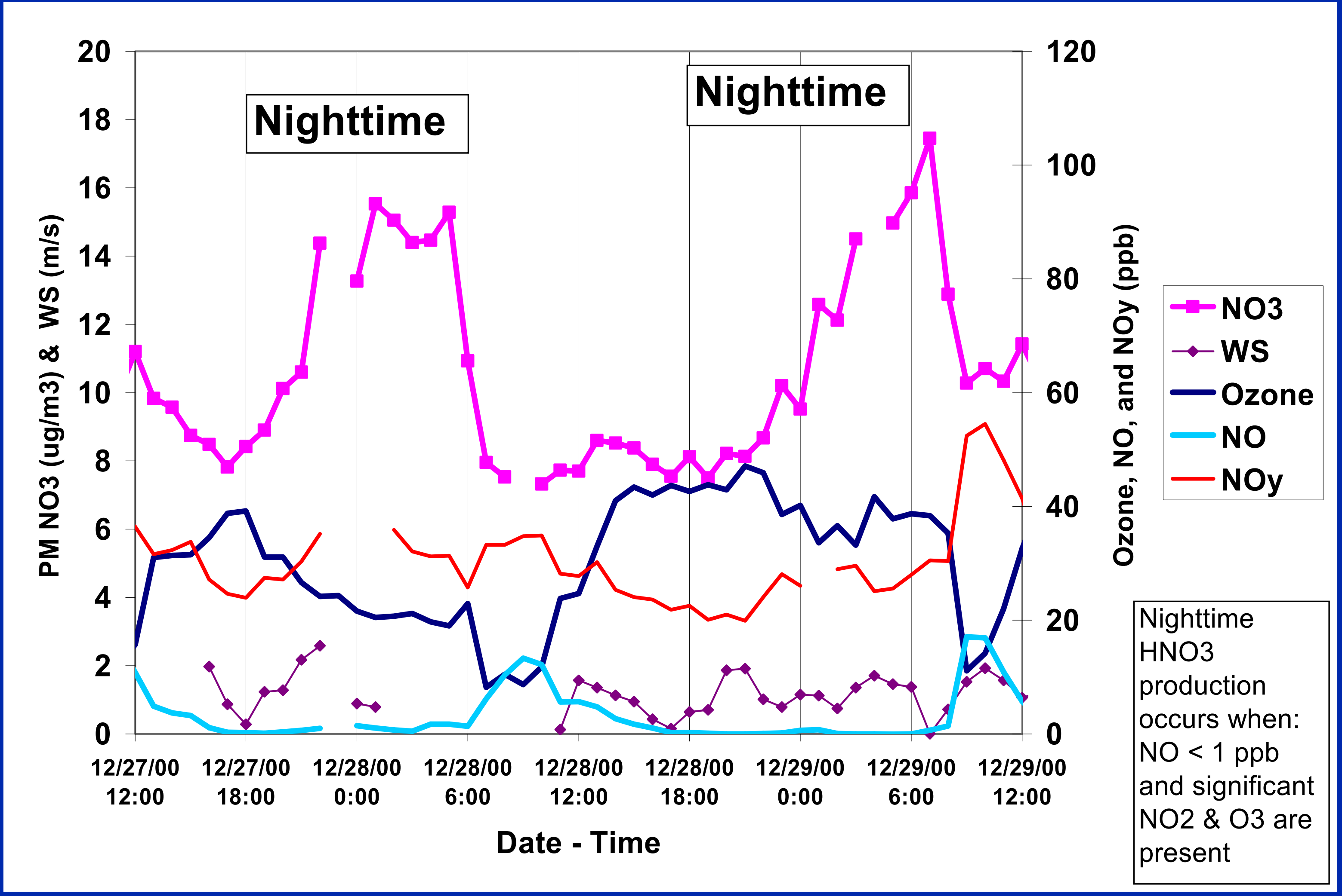
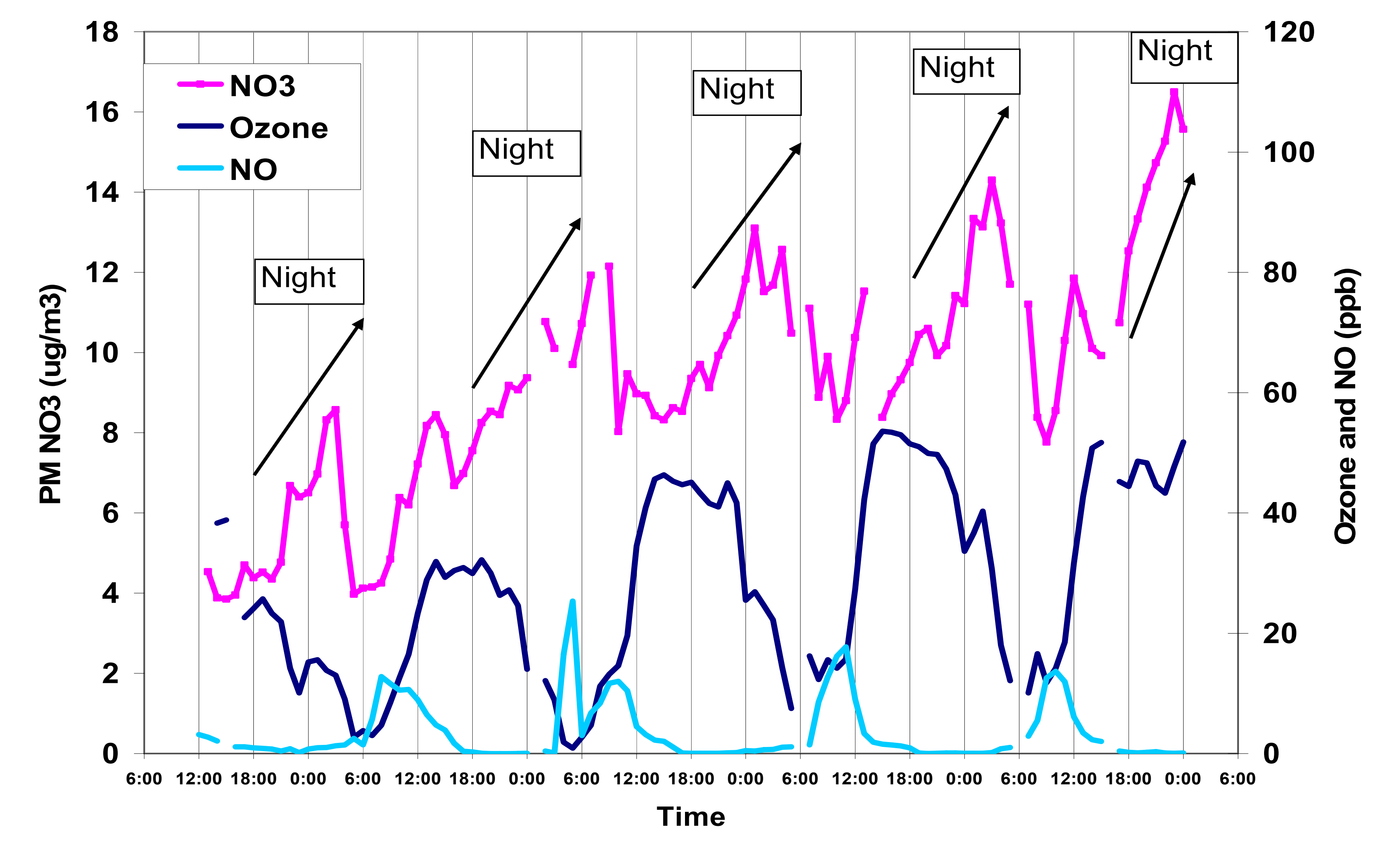


Nighttime Nitrate Production Aloft
Angiola Tower - 90m Data 12/27/00 – 12/29/00

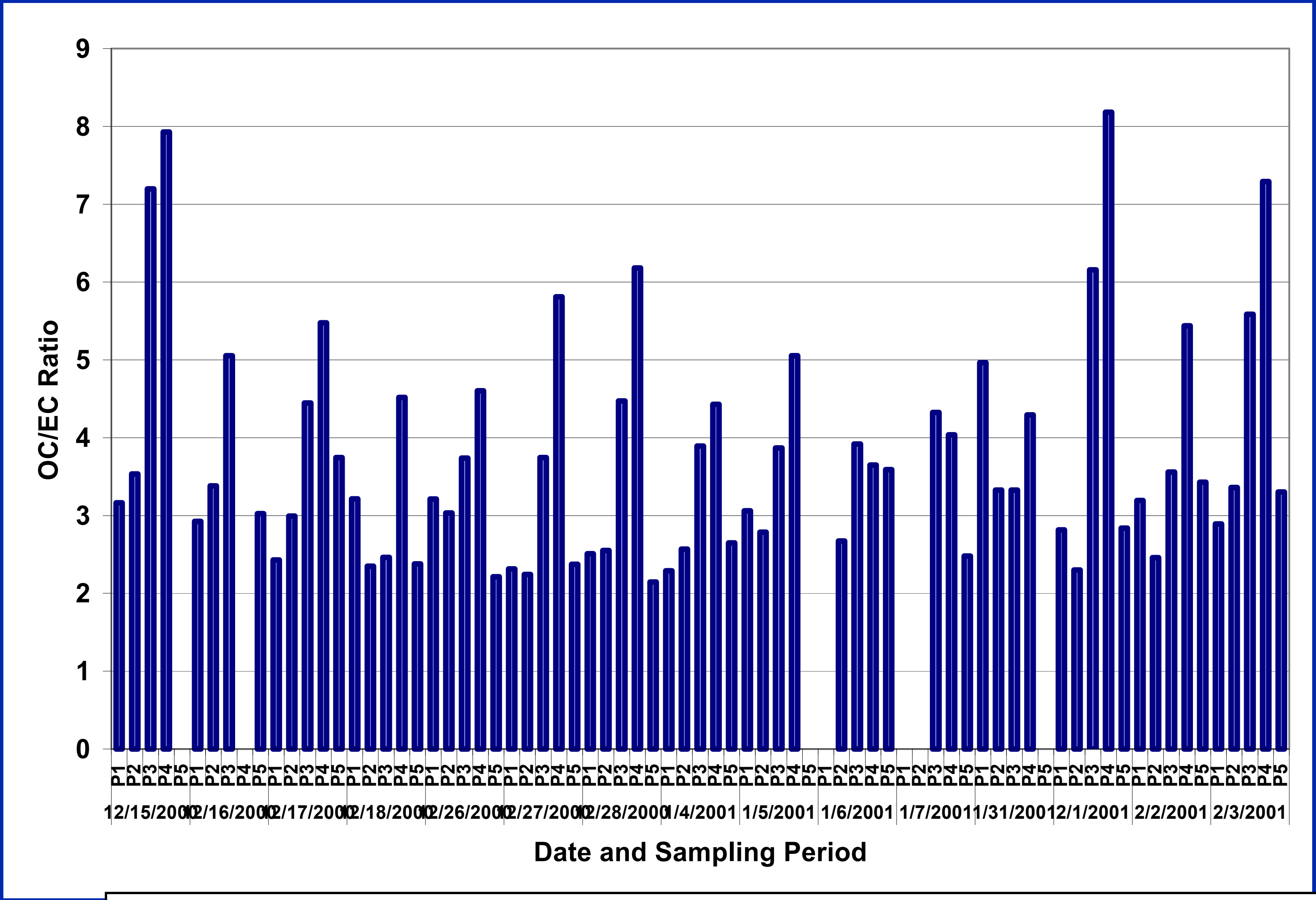


Nighttime HNO3 production occurs when: NO < 1 ppb and significant NO2 & O3 are present

Nighttime Nitrate Production Aloft
Angiola Tower - 90m Data 1/30/01 – 2/4/01



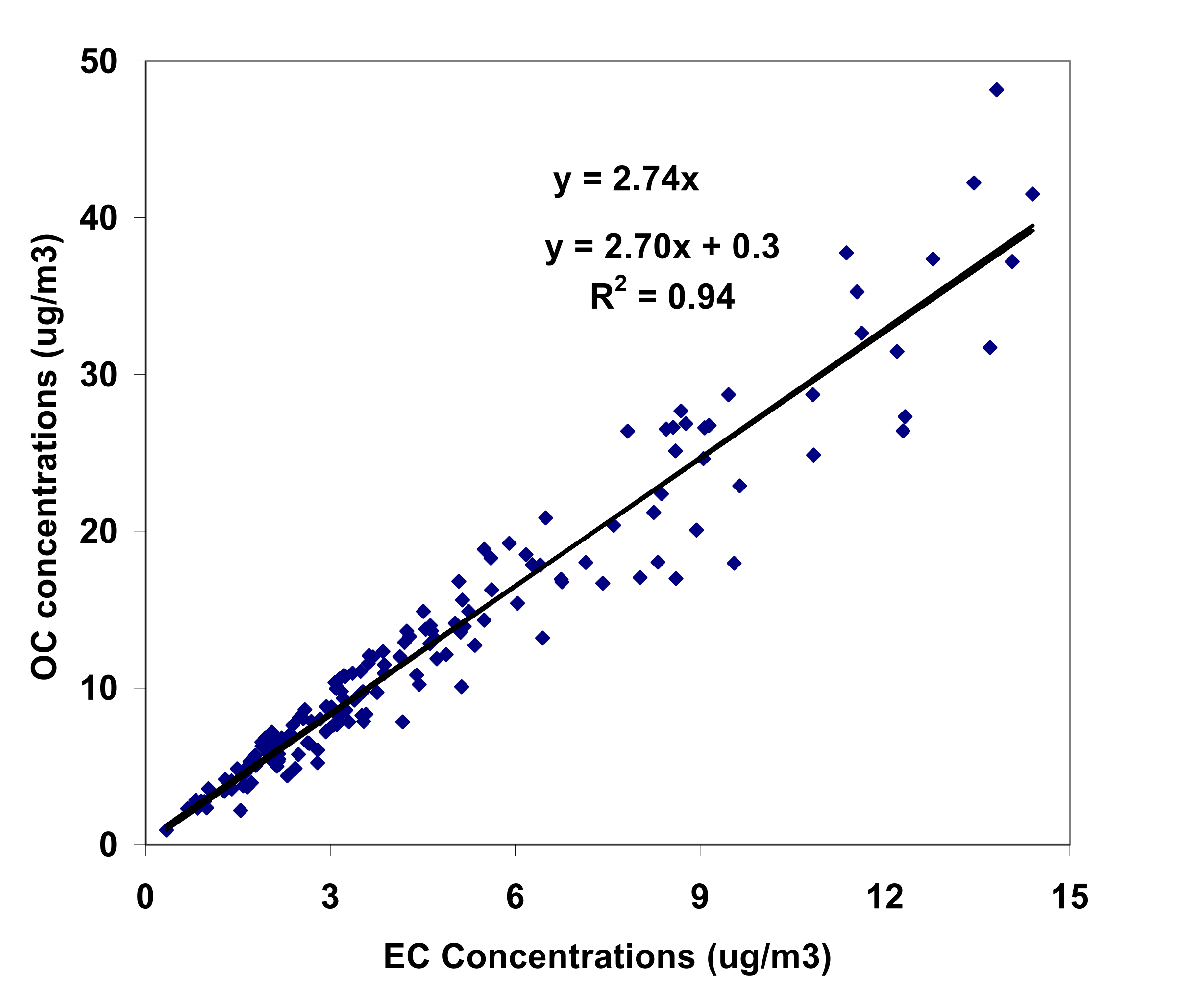
OC/EC Ratios at Bakersfield on IOP Days



OC/EC ratios increase during the day

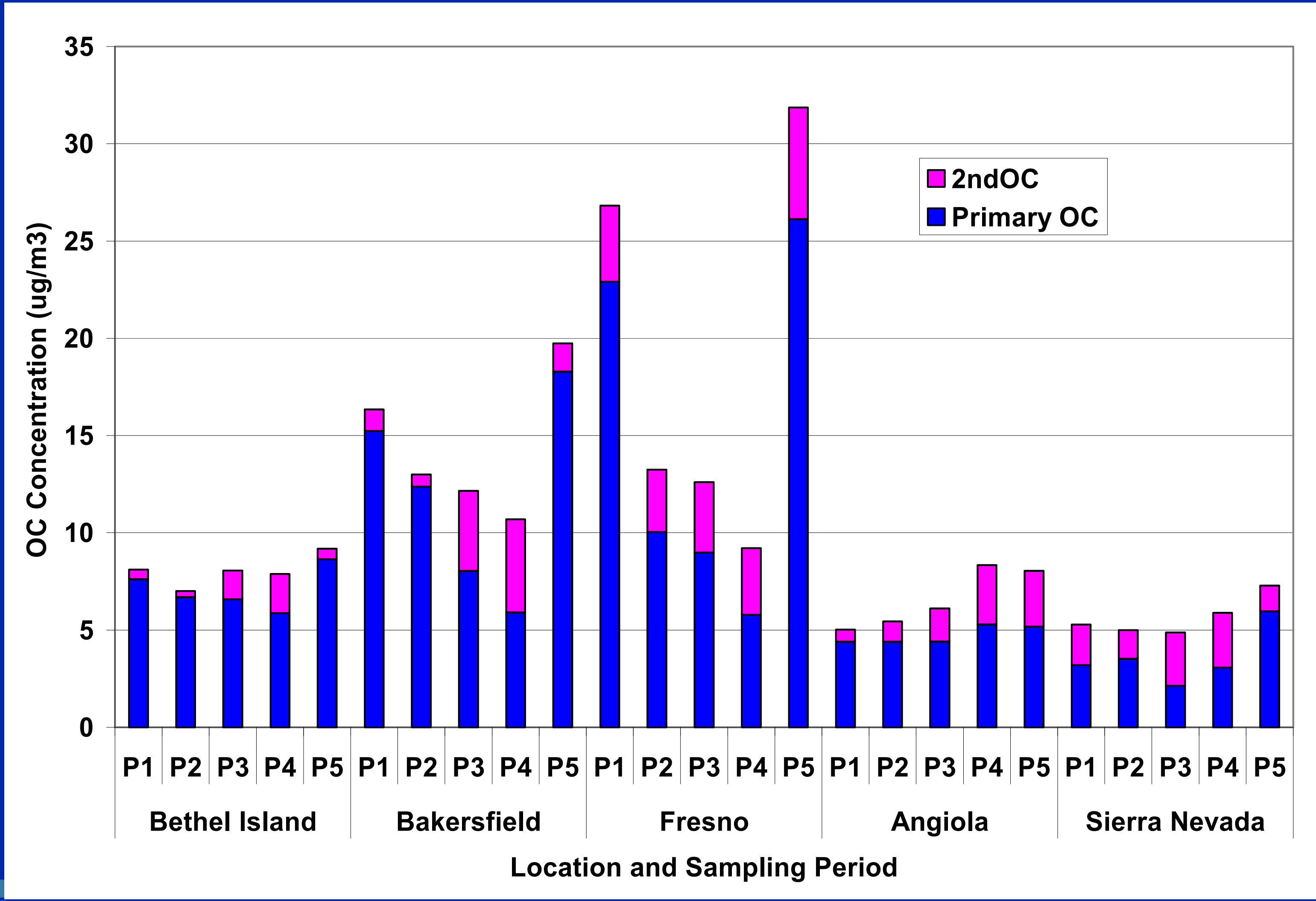
Periods: P1 = 0-5, P2 = 5-10, P3 = 10-13, P4 = 13-16, P5 = 16 -24

Comparison of OC and EC When OC/EC < 3.5 Fresno, Bakersfield, Bethel Island, Angiola



Purpose: Establish the OC/EC ratio of primary emissions

Estimated Average Primary and Secondary OC on IOP Days



Average Percent Secondary OC (of Total OC)

Location	Primary OC/EC = 2.74	Primary OC/EC = 3.00
Bethel Island	15%	11%
Bakersfield	22%	17%
Fresno	23%	18%
Angiola	25%	21%
Sierra Nevada	39%	34%

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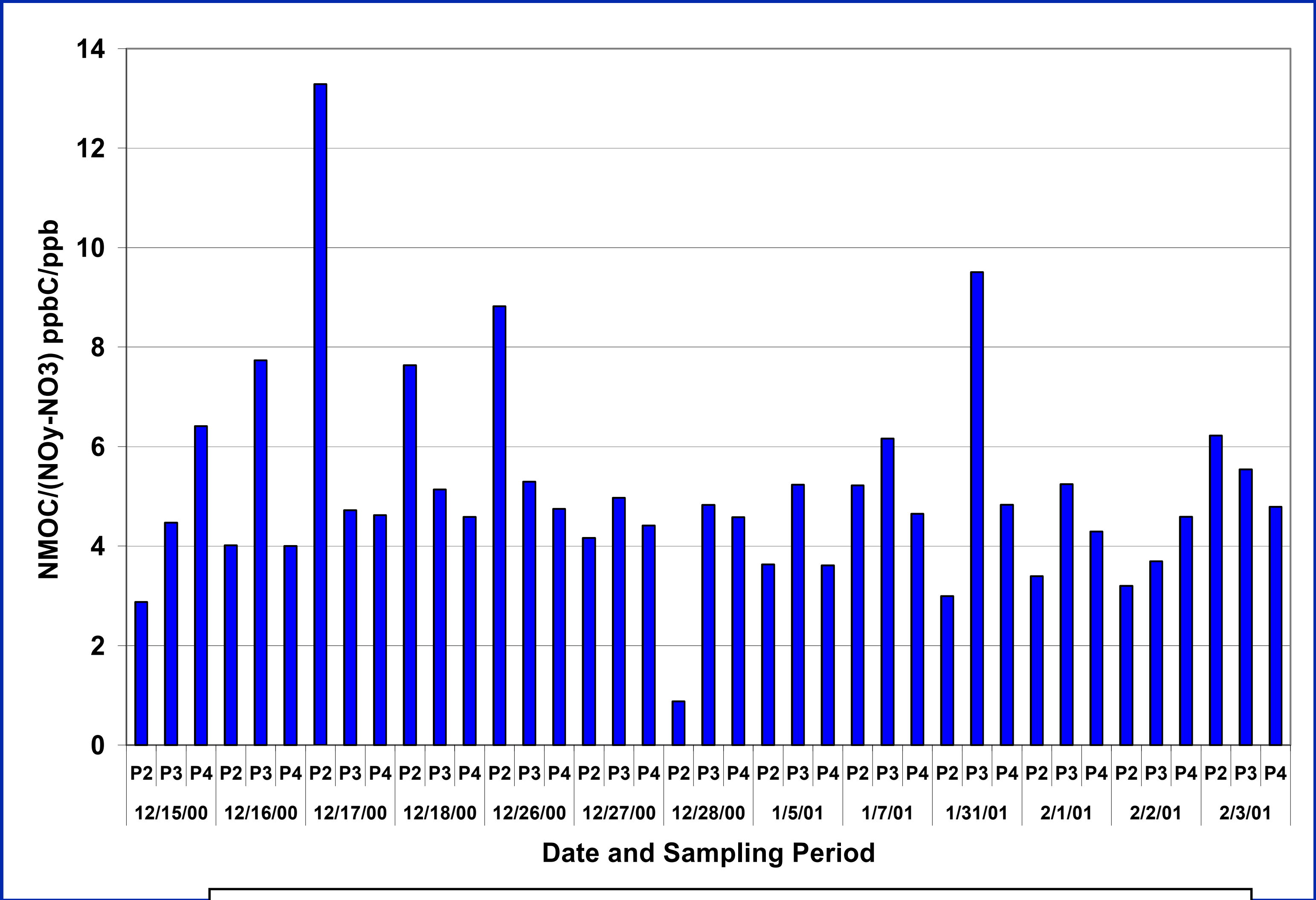
NMOC/(NO_y-NO_3) Ratios in Fresno Winter IOP Days



NO_x ~ NO_y-NO_3

Ratios <8 indicates VOC-NO_x oxidation is in the VOC- and sunlight-limited regime

Periods: P2 = 5-10 P3 = 10-16 P4 = 16-24

Conclusions

- Particulate NO_3 and OC concentrations are small relative to gaseous NO_y and NMOC precursor concentrations.
- Particulate NH_4NO_3 concentrations are limited by the rate of HNO_3 formation, rather than by the availability of NH_3.
- HNO_3 is formed via both daytime photochemistry and aloft nighttime chemistry.
- Primary NO_x and OC+EC emissions are important contributors; high nighttime OC+EC emissions are evident, especially in Fresno.
- Secondary organic aerosol formation from VOC emissions may account for 15% to 25% of the total OC.
- Relatively low NMOC/NO_x ratios indicate the daytime photochemistry is VOC-, sunlight-, and background-ozone-limited in winter. This is a nonlinear regime for the gas-phase chemistry.